

SUMMARY PROBLEM

- (a) (1) $\text{HNic}(aq) \rightleftharpoons \text{H}^+(aq) + \text{Nic}^-(aq)$ $K_a = 1.4 \times 10^{-5}$
- $\text{H}^+(aq) + \text{OH}^-(aq) \rightleftharpoons \text{H}_2\text{O}$ $\frac{1}{K_w} = \frac{1}{1.0 \times 10^{-14}}$
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- $\text{HNic}(aq) + \text{OH}^-(aq) \rightleftharpoons \text{Nic}^-(aq) + \text{H}_2\text{O}$ $K = 1.4 \times 10^{-9}$
- (2) $\text{Nic}^-(aq) + \text{H}^+(aq) \rightleftharpoons \text{HNic}(aq)$ $K = \frac{1}{K_a} = \frac{1}{1.4 \times 10^{-5}} = 7.1 \times 10^4$
- (3) $\text{HNic}(aq) \rightleftharpoons \text{H}^+(aq) + \text{Nic}^-(aq)$ $K_a = 1.4 \times 10^{-5}$
- $\text{H}^+(aq) + \text{F}^-(aq) \rightleftharpoons \text{HF}(aq)$ $\frac{1}{K_a} = \frac{1}{6.9 \times 10^{-4}}$
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- $\text{HNic}(aq) + \text{F}^-(aq) \rightleftharpoons \text{HF}(aq) + \text{Nic}^-(aq)$ $K = 0.020$
- (b) (1) $\text{mol HNic} = 0.295 \text{ mol/L} \times (1.25 \text{ L}) = 0.369$ $\text{mol Nic}^- = 47.13 \text{ g} \times \frac{1 \text{ mol}}{145.1 \text{ g}} = 0.325$
- $[\text{H}^+] = 1.4 \times 10^{-5} \times \frac{0.369}{0.325} = 1.6 \times 10^{-5}; \text{ pH} = 4.80$
- (2) H^+ reacts with Nic^- to produce more HNic ; Nic^- is used up.
- $[\text{H}^+] = 1.4 \times 10^{-5} \times \frac{0.369 + 0.100}{0.325 - 0.100} = 2.9 \times 10^{-5}; \text{ pH} = 4.53$
- (3) $\text{mol OH}^- = 5.00 \text{ g} \times \frac{1 \text{ mol}}{40.0 \text{ g}} = 0.125$
- OH^- reacts with HNic to produce more Nic^- ; HNic is used up.
- $[\text{H}^+] = 1.4 \times 10^{-5} \times \frac{0.369 - 0.125}{0.325 + 0.125} = 7.6 \times 10^{-6}; \text{ pH} = 5.11$
- (4) $\text{mol H}^+ = 0.095 \text{ L} \times (5.00 \text{ mol/L}) = 0.475$
- H^+ reacts with Nic^- ; Nic^- is limiting, so it is consumed.
- H^+ left over from reaction $= 0.475 - 0.325 = 0.150$; H^+ contribution of HNic is negligible.
- $[\text{H}^+] = \frac{0.150 \text{ mol}}{0.095 \text{ L} + 1.25 \text{ L}} = 0.112 \text{ M}; \text{ pH} = 0.95$
- (5) Let x = the number of moles of HNic used by reacting with OH^- = number of moles of Nic^-
- $[\text{H}^+] = 10^{-5.50} = 3.16 \times 10^{-6}$
- $3.16 \times 10^{-6} = 1.4 \times 10^{-5} \times \frac{0.369 - x}{0.325 + x} \quad x = 0.24$
- 0.24 mol HNic must react with 0.24 mol OH^- .
- mass $\text{NaOH} = 0.24 \text{ mol} \times (40.0 \text{ g/mol}) = 9.6 \text{ g}$

$$(c) (1) 1.4 \times 10^{-5} = \frac{[H^+]^2}{0.575 - [H^+]}. \text{ Assume } [H^+] \ll 0.575; [H^+] = 2.8 \times 10^{-3}$$

$$\% \text{ ionization} = \frac{2.8 \times 10^{-3}}{0.575} \times 100 < 5\%; \text{ so the assumption is valid.} \quad \text{pH} = 2.55$$

$$(2) \text{ mol HNic} = 0.040 \text{ L} \times 0.575 \text{ mol/L} = 0.0230 = \text{moles OH}^- \text{ required}$$

$$0.023 \text{ mol OH}^- = 0.0230 \text{ mol KOH} \times \frac{1 \text{ L}}{0.335 \text{ mol}} = 0.0687 \text{ L} = 68.7 \text{ mL}$$

$$(3) \text{ At half neutralization; } [H^+] = K_a = 1.4 \times 10^{-5}; \quad \text{pH} = 4.85$$

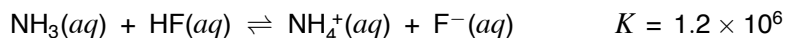
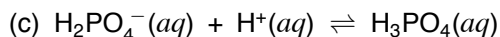
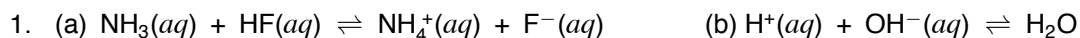
$$(4) \text{ At equivalence point: } V = (0.0687 + 0.0400) \text{ L} = 0.1087 \text{ L}$$

$$\text{mol Nic}^- = \text{mol HNic} = 0.0230; \quad [\text{Nic}^-] = \frac{0.0230 \text{ mol}}{0.1087 \text{ L}} = 0.216 \text{ M}$$

$$7.1 \times 10^{-10} = \frac{[\text{OH}^-]^2}{0.216 - [\text{OH}^-]}; \quad \text{assume } [\text{OH}^-] \ll 0.216 \quad [\text{OH}^-] = 1.2 \times 10^{-5}$$

$$\% \text{ ionization} \ll 5\%; \quad \text{pOH} = 4.91; \quad \text{pH} = 9.08$$

PROBLEMS



$$(b) K = 1/K_W = 1.0 \times 10^{14}$$

$$(c) K = 1/K_a \text{HSO}_3^- = 1/(6.0 \times 10^{-8}) = 1.7 \times 10^7$$

$$(d) K = 1/K_W = 1.0 \times 10^{14}$$

$$7. (a) K = 1/K_a \text{HF} = 1/(6.9 \times 10^{-4}) = 1.4 \times 10^3$$

$$(b) K = 1/K_W = 1.0 \times 10^{14}$$

$$(c) K = 1/K_a \text{H}_3\text{PO}_4 = 1/(7.1 \times 10^{-3}) = 1.4 \times 10^2$$

$$9. [\text{H}^+] = K_a \times \frac{[\text{HLac}]}{[\text{Lac}^-]}; \quad [\text{H}^+] = 1.4 \times 10^{-4} \times \frac{[\text{HLac}]}{[\text{Lac}^-]}$$

$$(a) [\text{H}^+] = 1.4 \times 10^{-4} \times \frac{0.250}{0.250}; \quad [\text{H}^+] = 1.4 \times 10^{-4}; \quad \text{pH} = 3.85$$

$$(b) [\text{H}^+] = 1.4 \times 10^{-4} \times \frac{0.250}{0.125}; \quad [\text{H}^+] = 2.8 \times 10^{-4}; \quad \text{pH} = 3.55$$

$$(c) [\text{H}^+] = 1.4 \times 10^{-4} \times \frac{0.250}{0.0800}; \quad [\text{H}^+] = 4.4 \times 10^{-4}; \quad \text{pH} = 3.36$$

$$(d) [\text{H}^+] = 1.4 \times 10^{-4} \times \frac{0.250}{0.0500}; \quad [\text{H}^+] = 7.0 \times 10^{-4}; \quad \text{pH} = 3.15$$

$$11. [\text{H}^+] = K_a \times \frac{n_{\text{HA}}}{n_{\text{A}^-}}; \quad [\text{H}^+] = K_a \times \frac{\text{mol HNO}_2}{\text{mol NO}_2^-}; \quad [\text{H}^+] = 6.0 \times 10^{-4} \times \frac{(0.2500 \text{ L})(0.0410 \text{ mol/L})}{0.0250 \text{ mol}}$$

$$[\text{H}^+] = 2.5 \times 10^{-4}; \quad \text{pH} = 3.61$$

$$13. (a) \text{mol HC}_2\text{H}_3\text{O}_2 = \frac{12.50 \text{ g}}{60.1 \text{ g/mol}} = 0.208; \quad \text{mol C}_2\text{H}_3\text{O}_2^- = \frac{15.00 \text{ g}}{82.0 \text{ g/mol}} = 0.183$$

$$[\text{H}^+] = 1.8 \times 10^{-5} \times \frac{0.208}{0.183} = 2.0 \times 10^{-5}; \quad \text{pH} = 4.70$$

$$(b) \text{pH} = 4.70$$

$$15. \text{Find } K_b: \quad \text{pH} = 8.73; \quad [\text{H}^+] = 1.9 \times 10^{-9} \text{ M}; \quad [\text{OH}^-] = (1.0 \times 10^{-14})/(1.9 \times 10^{-9}) = 5.3 \times 10^{-6} \text{ M}$$

$$[\text{X}^-] = [\text{NaX}] = 0.614 \text{ mol}/2.50 \text{ L} = 0.246 \text{ M}$$

$$K_b = \frac{[\text{OH}^-]^2}{[\text{X}^-]} = \frac{(5.3 \times 10^{-6})^2}{0.246} = 1.14 \times 10^{-10}$$

$$\text{Find } K_a: \quad K_a = (1.0 \times 10^{-14})/(1.14 \times 10^{-10}) = 8.8 \times 10^{-5}$$

$$[\text{H}^+] = K_a \times \frac{\text{mol HX}}{\text{mol X}^-} = 8.8 \times 10^{-5} \times \frac{0.219}{0.614} = 3.1 \times 10^{-5}; \quad \text{pH} = 4.50$$

$$17. \text{mol SnF}_2 = (0.250 \text{ L})(0.150 \text{ mol/L}) = 0.0375; \quad \text{mol F}^- = 2(\text{mol SnF}_2) = 0.0750$$

$$(a) 0.0750 \text{ mol F}^- + 0.100 \text{ mol H}^+; \quad \text{no buffer; all the F}^- \text{ is used up}$$

$$(b) 0.060 \text{ mol H}^+ \text{ produces } 0.060 \text{ mol HF and uses up } 0.0150 \text{ mol F}^-$$

$$\text{Resulting solution: } 0.060 \text{ mol HF} + 0.0150 \text{ mol F}^-$$

Solution is a buffer.

(c) 0.040 mol H^+ produces 0.040 mol HF and uses up 0.040 mol F^- .

Resulting solution: 0.040 mol HF + 0.0350 mol F^- .

Solution is a buffer.

(d) No. The resulting solution has a strong base, NaOH and a weak base F^- .

(e) Yes. The resulting solution has 0.040 mol HF and 0.0750 mol F^- .

$$19. \text{ mol HOBr} = (2.50 \text{ g})(1 \text{ mol}/96.9 \text{ g}) = 0.0258$$

$$\text{mol OH}^- = \text{mol KOH} = (0.750 \text{ g})(1 \text{ mol}/56.1 \text{ g}) = 0.0134$$

The reaction between HOBr and KOH produces 0.0134 mol OBr^- and leaves 0.0124 mol HOBr.

$$[\text{H}^+] = 2.5 \times 10^{-9} \times \frac{0.0124}{0.0134} = 2.3 \times 10^{-9}; \quad \text{pH} = 8.64$$

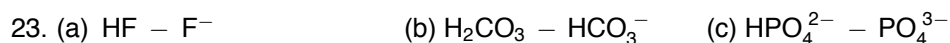
$$21. \text{ mol HC}_4\text{H}_7\text{O}_2 = (2.00 \text{ g})(1 \text{ mol}/88.1 \text{ g}) = 0.0227$$

$$\text{mol OH}^- = \text{mol NaOH} = (0.50 \text{ g})(1 \text{ mol}/40.0 \text{ g}) = 0.0125$$

The reaction between $\text{HC}_4\text{H}_7\text{O}_2$ and OH^- produces 0.0125 mol $\text{C}_4\text{H}_7\text{O}_2^-$.

$$\text{mol HC}_4\text{H}_7\text{O}_2 \text{ unreacted} = 0.0227 - 0.0125 = 0.0102$$

$$[\text{H}^+] = 1.5 \times 10^{-5} \times \frac{0.0102}{0.0125} = 1.2 \times 10^{-5}; \quad \text{pH} = 4.91$$



$$25. \text{ pH} = 9.40; \quad [\text{H}^+] = 4.0 \times 10^{-10} \text{ M}$$

$$(a) 4.0 \times 10^{-10} = 4.7 \times 10^{-11} \times \frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]}; \quad \text{ratio} = \frac{4.0 \times 10^{-10}}{4.7 \times 10^{-11}} = 8.5$$

$$(b) \text{ mol CO}_3^{2-} = \text{mol Na}_2\text{CO}_3 = (1.00 \text{ L})(0.225 \text{ mol/L}) = 0.225$$

$$\frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = \frac{\text{mol HCO}_3^-}{\text{mol CO}_3^{2-}}; \quad 8.5 = \frac{\text{mol HCO}_3^-}{0.225}; \quad \text{mol HCO}_3^- = 1.9$$

$$(c) \text{ mol HCO}_3^- = (0.475 \text{ L})(0.336 \text{ mol/L}) = 0.160$$

$$8.5 = \frac{0.160}{\text{mol CO}_3^{2-}}; \quad \text{mol CO}_3^{2-} = 0.0188; \quad \text{mol Na}_2\text{CO}_3 = \text{mol CO}_3^{2-}$$

$$\text{mass Na}_2\text{CO}_3 = (0.0188 \text{ mol})(106 \text{ g/mol}) = 2.0 \text{ g}$$

$$(d) \text{ mol CO}_3^{2-} = \text{mol Na}_2\text{CO}_3 = (0.735 \text{ L})(0.139 \text{ mol/L}) = 0.102$$

$$8.5 = \frac{\text{mol HCO}_3^-}{0.102} ; \quad \text{mol HCO}_3^- = 0.86 ; \quad \text{mol Na}_2\text{CO}_3 = \text{mol CO}_3^{2-}$$

$$V = 0.86 \text{ mol} \times \frac{1 \text{ L}}{0.200 \text{ mol}} = 4.3 \text{ L}$$

27.	Base	Acid
(a)	0.250 <i>M</i>	0.250 <i>M</i>
(b)	0.250 <i>M</i>	0.125 <i>M</i>
(c)	0.250 <i>M</i>	0.0800 <i>M</i>
(d)	0.250 <i>M</i>	0.0500 <i>M</i>

$$29. \text{ mol H}_2\text{PO}_4^- = \text{mol KH}_2\text{PO}_4 = (0.300 \text{ L})(0.500 \text{ mol/L}) = 0.150$$

$$\text{mol HPO}_4^{2-} = \text{mol K}_2\text{HPO}_4 = (0.300 \text{ L})(0.317 \text{ mol/L}) = 0.0951$$

$$(a) [\text{H}^+] = 6.2 \times 10^{-8} \times \frac{\text{mol H}_2\text{PO}_4^-}{\text{mol HPO}_4^{2-}} = 6.2 \times 10^{-8} \times \frac{0.150}{0.0951} = 9.8 \times 10^{-8} ; \quad \text{pH} = 7.01$$

$$(b) \text{ HCl (H}^+) \text{ reacts with HPO}_4^{2-} \text{ to use up 0.0500 mol HPO}_4^{2-} \text{ and make 0.0500 mol H}_2\text{PO}_4^-.$$

$$\text{mol H}_2\text{PO}_4^- = 0.150 + 0.0500 = 0.200 ; \quad \text{mol HPO}_4^{2-} = 0.0951 - 0.0500 = 0.0451$$

$$[\text{H}^+] = 6.2 \times 10^{-8} \times \frac{\text{mol H}_2\text{PO}_4^-}{\text{mol HPO}_4^{2-}} = 6.2 \times 10^{-8} \times \frac{0.200}{0.0451} = 2.7 \times 10^{-7} ; \quad \text{pH} = 6.56$$

$$(c) \text{ NaOH (OH}^-) \text{ reacts with H}_2\text{PO}_4^- \text{ to use up 0.0500 mol H}_2\text{PO}_4^- \text{ and make 0.0500 mol HPO}_4^{2-}.$$

$$\text{mol H}_2\text{PO}_4^- = 0.150 - 0.0500 = 0.100 ; \quad \text{mol HPO}_4^{2-} = 0.0951 + 0.0500 = 0.1451$$

$$[\text{H}^+] = 6.2 \times 10^{-8} \times \frac{\text{mol H}_2\text{PO}_4^-}{\text{mol HPO}_4^{2-}} = 6.2 \times 10^{-8} \times \frac{0.100}{0.1451} = 4.3 \times 10^{-8} ; \quad \text{pH} = 7.37$$

$$31. (a) \text{ mol H}_2\text{PO}_4^- = \text{mol KH}_2\text{PO}_4 = (10.0 \text{ L})(0.500 \text{ mol/L}) = 5.00$$

$$\text{mol HPO}_4^{2-} = \text{mol K}_2\text{HPO}_4 = (10.0 \text{ L})(0.317 \text{ mol/L}) = 3.17$$

$$[\text{H}^+] = 6.2 \times 10^{-8} \times \frac{\text{mol H}_2\text{PO}_4^-}{\text{mol HPO}_4^{2-}} = 6.2 \times 10^{-8} \times \frac{5.00}{3.17} = 9.8 \times 10^{-8} ; \quad \text{pH} = 7.01$$

(b) Before dilution (from Problem 29):

$$\text{mol H}_2\text{PO}_4^- = \text{mol KH}_2\text{PO}_4 = (0.300 \text{ L})(0.500 \text{ mol/L}) = 0.150$$

$$\text{mol HPO}_4^{2-} = \text{mol K}_2\text{HPO}_4 = (0.300 \text{ L})(0.317 \text{ mol/L}) = 0.0951$$

After dilution to 10.0 L, and taking 0.600 L of the buffer:

$$\text{mol H}_2\text{PO}_4^- = \frac{0.150 \text{ mol}}{10.0 \text{ L}} \times 0.600 \text{ L} = 0.00900 \text{ mol}$$

$$\text{mol HPO}_4^{2-} = \frac{0.0951 \text{ mol}}{10.0 \text{ L}} \times 0.600 \text{ L} = 0.005571 \text{ mol}$$

H^+ added = 0.0500 mol; HPO_4^{2-} is limiting and used up. Mol H^+ left = 0.0500 – 0.00571 = 0.0443

$$[\text{H}^+] = 0.0443 \text{ mol}/0.600 \text{ L} = 0.0738 \text{ M}; \quad \text{pH} = 1.13$$

(c) as in (b): mol $\text{H}_2\text{PO}_4^- = 0.00900$; mol $\text{HPO}_4^{2-} = 0.00571$

mol OH^- added = 0.0500; H_2PO_4^- is limiting and used up.

$$\text{mol OH}^- \text{ left} = 0.0500 - 0.0090 = 0.0410$$

$$[\text{OH}^-] = 0.0410 \text{ mol}/0.600 \text{ L} = 0.0683 \text{ M}; \quad \text{pOH} = 1.17; \quad \text{pH} = 12.83$$

(d) (a) is the same; (b) and (c) vary.

(e) Dilution does not change the pH of a buffer but reduces buffer capacity.

$$33. (a) [\text{H}^+] = K_a \text{H}_2\text{PO}_4^- \times \frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]} = 6.2 \times 10^{-8} \times 3.0 = 1.86 \times 10^{-7}; \quad \text{pH} = 6.73$$

(b) ratio of acid to base is 3:1. Using up 15% of base (HPO_4^{2-}) means:

$$\text{mol HPO}_4^{2-} = 1 - (0.15 \times 1) = 0.85; \quad \text{mol H}_2\text{PO}_4^- = 3 + (0.15 \times 1) = 3.15$$

$$[\text{H}^+] = 6.2 \times 10^{-8} \times \frac{3.15}{0.85} = 2.30 \times 10^{-7} \text{ M}; \quad \text{pH} = 6.64$$

$$(c) [\text{H}^+] = 1.0 \times 10^{-7} \text{ M}; \quad 1.0 \times 10^{-7} = 6.2 \times 10^{-8} \times \frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]}; \quad \frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]} = 1.6$$

$$35. \text{pH} = 7.40; \quad [\text{H}^+] = 4.0 \times 10^{-8}$$

$$(a) \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = \frac{[\text{H}^+]}{K_a \text{H}_2\text{CO}_3} = \frac{4.0 \times 10^{-8}}{4.4 \times 10^{-7}} = 0.091$$

$$(b) \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = \frac{0.091}{1} ; \quad \text{Assume } [\text{HCO}_3^-] = 1.000 \text{ M, then } [\text{H}_2\text{CO}_3] = 0.091 \text{ M}$$

$$[\text{HCO}_3^-] \text{ after conversion to } \text{H}_2\text{CO}_3 = 1.000 - (0.15 \times 1.000) = 0.85 \text{ M}$$

$$[\text{H}_2\text{CO}_3] \text{ after conversion} = 0.091 + (0.15 \times 1.000) = 0.241 \text{ M}$$

$$[\text{H}^+] = 4.4 \times 10^{-7} \frac{0.241}{0.85} = 1.25 \times 10^{-7} ; \quad \text{pH} = 6.90$$

$$(c) \text{ From (a) assume } [\text{HCO}_3^-] = 1.000 \text{ M, then } [\text{H}_2\text{CO}_3] = 0.091 \text{ M}$$

$$[\text{H}_2\text{CO}_3] \text{ after conversion} = 0.091 - (0.15 \times 0.091) = 0.077 \text{ M}$$

$$[\text{HCO}_3^-] \text{ after conversion} = 1.000 + (0.15 \times 0.091) = 1.014 \text{ M}$$

$$[\text{H}^+] = 4.4 \times 10^{-7} \times \frac{0.077}{1.014} = 3.34 \times 10^{-8} \text{ M} ; \quad \text{pH} = 7.48$$

37. (a) MO

(b) PP

(c) any

(d) MO

39. (a) $\text{p}K_a = 8.2 ; \quad K_a = 6.3 \times 10^{-9}$

(b) 7.2 – 9.2

(c) purple

$$41. (a) \text{ mol OH}^- = 2(\text{mol Sr(OH)}_2) = 2[(0.0584 \text{ L})(0.218 \text{ mol/L})] = 0.0255$$

$$\text{mol H}^+ = \text{mol HNO}_3 = \text{mol OH}^- = 0.0255$$

$$[\text{H}^+] = [\text{HNO}_3] = 0.0255 \text{ mol}/0.02500 \text{ L} = 1.02 \text{ M} ; \quad \text{pH} = 8.6 \times 10^{-3}$$

(b) 7.00

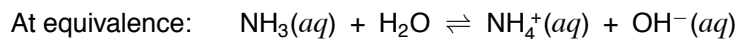
$$(c) \text{ mol NO}_3^- = \text{mol HNO}_3 = 0.0255 ; \quad [\text{NO}_3^-] = \frac{0.0255 \text{ mol}}{(0.02500 + 0.0584) \text{ L}} = 0.305 \text{ M}$$

$$\text{mol Sr}^{2+} = \frac{1}{2}(\text{mol OH}^-) = \frac{0.0255}{2} ; \quad [\text{OH}^-] = \frac{(0.0255/2) \text{ mol}}{(0.02500 + 0.0584) \text{ L}} = 0.153 \text{ M}$$

$$43. (a) \text{ mol NH}_4^+ = \text{mol NH}_4\text{Cl} = (25.00 \text{ g})(1 \text{ mol}/53.49 \text{ g}) = 0.467$$

$$\text{mol OH}^- = \text{mol KOH} = \text{mol NH}_4^+ = 0.467 ; \quad V_{\text{KOH}} = (0.467 \text{ mol})(1 \text{ L}/0.114 \text{ mol}) = 4.10 \text{ L}$$

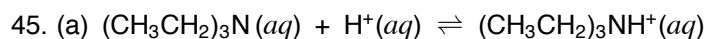
$$(b) [\text{Cl}^-] = [\text{K}^+] = [\text{NH}_3] = \frac{0.467 \text{ mol}}{4.10 \text{ L} + 0.178 \text{ L}} = 0.109 \text{ M}$$



$$K_b = \frac{[\text{OH}^-]^2}{[\text{NH}_3] - [\text{OH}^-]} ; \quad \text{assume } [\text{OH}^-] \ll [\text{NH}_3]$$

$$1.8 \times 10^{-5} = \frac{[\text{OH}^-]^2}{0.109} ; \quad [\text{OH}^-] = 1.40 \times 10^{-3} ; \quad \% \text{ ionization} = 1.28 ; \quad \text{assumption valid}$$

(c) $\text{pOH} = 2.85 ; \quad \text{pH} = 11.15$



(b) $\text{mol H}^+ = \text{mol } (\text{CH}_3\text{CH}_2)_3\text{N} = (0.0200 \text{ L})(0.220 \text{ mol/L}) = 0.00440$

$\text{mol HCl} = \text{mol H}^+ = 0.00440$; $V_{\text{HCl}} = (0.00440 \text{ mol})(1 \text{ L}/0.544 \text{ mol}) = 0.00809 \text{ L}$

(c) $\text{mol Cl}^- = \text{mol H}^+ = \text{mol } (\text{CH}_3\text{CH}_2)_3\text{NH}^+ = 0.00440$

$$[\text{Cl}^-] = [(\text{CH}_3\text{CH}_2)_3\text{NH}^+] = \frac{0.00440 \text{ mol}}{(0.00809 + 0.0200) \text{ L}} = 0.157 \text{ M}$$

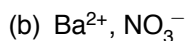
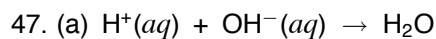
$$K_a (\text{CH}_3\text{CH}_2)_3\text{NH}^+ = \frac{1.0 \times 10^{-14}}{K_b} = \frac{1.0 \times 10^{-14}}{5.2 \times 10^{-4}} = 1.9 \times 10^{-11}$$

$[\text{H}^+] = [(\text{CH}_3\text{CH}_2)_3\text{N}]$; assume $[\text{H}^+] \ll [(\text{CH}_3\text{CH}_2)_3\text{NH}^+]$

$$1.9 \times 10^{-11} = \frac{[\text{H}^+]^2}{0.157} ; \quad [\text{H}^+] = 1.7 \times 10^{-6} ; \quad \% \text{ ionization} = 0.0011 ; \quad \text{assumption valid}$$

$[\text{H}^+] = [(\text{CH}_3\text{CH}_2)_3\text{N}] = 1.7 \times 10^{-6} \text{ M}$

(d) $\text{pH} = 5.77$



(c) $\text{mol OH}^- = 2(\text{mol Ba}(\text{OH})_2) = 2[(0.0500 \text{ L})(0.237 \text{ mol/L})] = 0.0237$

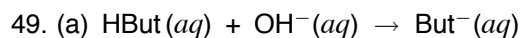
$\text{mol OH}^- = \text{mol H}^+ = \text{mol HNO}_3 = 0.0237$; $V_{\text{HNO}_3} = (0.0237 \text{ mol})(1 \text{ L}/0.4000 \text{ mol}) = 0.0592 \text{ L}$

(d) $[\text{OH}^-] = 2[\text{Ba}(\text{OH})_2] = 2(0.237) = 0.474 \text{ M}$; $\text{pOH} = 0.324$; $\text{pH} = 13.68$

(e) $\text{mol OH}^- \text{ (half-way)} = \frac{1}{2}(0.0237) = 0.01185$

$V_{\text{tot}} \text{ (half-way)} = (0.05000)_{\text{from OH}^-} + \frac{1}{2}(0.0592)_{\text{from H}^+} = 0.0796 \text{ L}$

$[\text{OH}^-] \text{ (half-way)} = 0.01185 \text{ mol}/0.0796 \text{ L} = 0.149$; $\text{pOH} = 0.827$; $\text{pH} = 13.17$



(c) $\text{mol OH}^- = \text{mol HBut} = (0.0500 \text{ L})(0.350 \text{ mol/L}) = 0.0175$

$\text{mol NaOH} = \text{mol OH}^- = 0.0175$; $V_{\text{NaOH}} = (0.0175 \text{ mol})(1 \text{ L}/0.225 \text{ mol}) = 0.0778 \text{ L}$

(d) $K_a = \frac{[\text{H}^+][\text{But}^-]}{[\text{HBut}] - [\text{H}^+]}$; $[\text{H}^+] = [\text{But}^-]$; assume $[\text{H}^+] \ll [\text{HBut}]$

$$1.5 \times 10^{-5} = \frac{[\text{H}^+]^2}{0.350} ; \quad [\text{H}^+] = 2.29 \times 10^{-3} ; \quad \% \text{ ionization} = 0.65 ; \quad \text{assumption valid} ; \quad \text{pH} = 2.64$$

(e) At half-equivalence: $[H^+] = K_a = 1.5 \times 10^{-5}$; $pH = 4.82$

(f) At the equivalence point: Solution has 0.0175 mol But^- and a volume of $(0.0778 + 0.0500)$ L.

$$[But^-] = 0.0175 \text{ mol} / 0.1278 \text{ L} = 0.137 \text{ M}; \quad K_b = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-5}} = 6.7 \times 10^{-10}$$

$$K_b = \frac{[HBut][OH^-]}{[But^-] - [OH^-]}; \quad [HBut] = [OH^-]; \quad \text{assume } [OH^-] \ll [But^-]$$

$$6.7 \times 10^{-10} = \frac{[OH^-]^2}{0.137}; \quad [OH^-] = 9.6 \times 10^{-6}; \quad \% \text{ ionization} \ll 5\%; \quad \text{assumption valid}$$

$$pOH = 5.02; \quad pH = 8.98$$

51. (a) mass of solution = 30.0 g; mass $HClO = (30.0 \text{ g})(0.10) = 3.00 \text{ g}$

$$\text{mol } HClO = (3.00 \text{ g})(1 \text{ mol}/52.46 \text{ g}) = 0.0572; \quad [HClO]_0 = 0.0572 \text{ mol}/0.0300 \text{ L} = 1.91 \text{ M}$$

$$K_a = \frac{[H^+][ClO^-]}{[HClO] - [H^+]}; \quad [H^+] = [ClO^-]; \quad \text{assume } [H^+] \ll [HClO]$$

$$2.8 \times 10^{-8} = \frac{[H^+]^2}{1.91}; \quad [H^+] = 2.3 \times 10^{-4}; \quad \% \text{ ionization} \ll 5\%; \quad \text{assumption valid}; \quad pH = 3.64$$

(b) At half-equivalence: $[H^+] = K_a = 2.8 \times 10^{-8}$; $pH = 7.55$

(c) $(\text{mol } ClO^-)_{eq} = (\text{mol } HClO)_0 = 0.0572$; $\text{mol } KOH = \text{mol } OH^- = \text{mol } HClO = 0.0572$

$$V_{KOH} = (0.0572 \text{ mol})(1 \text{ L}/0.419 \text{ mol}) = 0.137 \text{ L}; \quad V_{tot} = (0.137 + 0.030) \text{ L} = 0.167 \text{ L}$$

$$[ClO^-] = 0.0572 \text{ mol}/0.167 \text{ L} = 0.343 \text{ M}$$

$$K_b = \frac{[HClO][OH^-]}{[ClO^-] - [OH^-]}; \quad [HClO] = [OH^-]; \quad \text{assume } [OH^-] \ll [ClO^-]$$

$$3.6 \times 10^{-7} = \frac{[OH^-]^2}{0.343}; \quad [OH^-] = 3.51 \times 10^{-4}; \quad \% \text{ ionization} = 0.102; \quad \text{assumption valid}$$

$$pOH = 3.45; \quad pH = 10.54$$

53. $pH = 4.50$; $[H^+] = 3.2 \times 10^{-5} \text{ M}$

$$\text{mol } Lac^- = \text{mol } NaLac = (250.0 \text{ g})(1 \text{ mol}/112.1 \text{ g}) = 2.230 \text{ mol}$$

$$[H^+] = K_a \frac{\text{mol } HLac}{\text{mol } Lac^-}; \quad \text{mol } HLac = \frac{(3.2 \times 10^{-5})(2.230)}{1.4 \times 10^{-4}} = 0.51$$

$$\text{mass } HLac = (0.51 \text{ mol})(90.1 \text{ g/mol}) = 46 \text{ g}; \quad \text{mass } HLac \text{ solution} = \frac{46 \text{ g}}{0.73} = 63 \text{ g}$$

$$\text{Volume } HLac \text{ solution} = (63 \text{ g})(1 \text{ mL}/1.20 \text{ g}) = 52 \text{ mL}$$

55. $\text{pH} = 2.95$; $[\text{H}^+] = 1.1 \times 10^{-3} \text{ M}$

$$K_a = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}] - [\text{H}^+]}$$
 ; $[\text{H}^+] = [\text{Ac}^-]$; assume $[\text{H}^+] \ll [\text{HAc}]$

$$1.8 \times 10^{-5} = \frac{(1.1 \times 10^{-3})^2}{[\text{HAc}]}$$
 ; $[\text{HAc}] = 0.067 \text{ M}$; % ionization $\ll 5\%$; assumption valid

Assume 1000.0 mL of "vinegar" = 1050.0 g of "vinegar" ; mass HAc = (0.067 mol)(60.0 g/mol) = 4.02 g

% HAc in "vinegar" = $(4.02/1050) \times 100\% = 0.38\%$. Solution *cannot* be called vinegar.

57. (a) $\text{mol OH}^- = \text{mol KOH} = (0.03262 \text{ L})(0.730 \text{ mol/L}) = 0.0238 \text{ mol}$

$$\text{mol HUr} = \text{mol OH}^- = 0.0238$$
 ; MM HUr = 4.00 g/0.0238 mol = 168 g/mol

(b) $\text{pH} = 4.12$; $[\text{H}^+] = 7.6 \times 10^{-5} \text{ M}$; $\text{mol OH}^- = \text{mol KOH} = (0.01200 \text{ L})(0.730 \text{ mol/L}) = 0.00876$

$$\text{mol Ur}^- \text{ formed} = \text{mol OH}^- = 0.00876$$
 ; $\text{mol HUr left} = 0.0238 - 0.00876 = 0.0150$

$$[\text{H}^+] = K_a \frac{\text{mol HUr}}{\text{mol Ur}^-}$$
 ; $7.6 \times 10^{-5} = K_a \frac{0.0150}{0.00876}$; $K_a = 4.4 \times 10^{-5}$

59. $\Pi = MRT$; $M = \frac{0.878 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})} = 0.0359 \text{ mol/L}$

$$\text{pH} = 6.76$$
 ; $[\text{H}^+] = 1.7 \times 10^{-7}$

$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}] - [\text{H}^+]}$$
 ; $[\text{H}^+] = [\text{X}^-]$; assume $1.7 \times 10^{-7} \ll 0.0359$

$$K_a = \frac{[\text{H}^+]^2}{[\text{HX}]} = \frac{(1.7 \times 10^{-7})^2}{0.0359} = 8.4 \times 10^{-13}$$
 ; $K_b = \frac{1.0 \times 10^{-14}}{8.4 \times 10^{-13}} = 0.012$

61. (a) 8 \square , 2 \bigcirc

(b) 5 \square , 5 \bigcirc (half-neutralization)

(c) 10 \bigcirc

(d) 10 \bigcirc , 2 \triangle

63. (a) weak

(b) at 25 mL, $\text{pH} \approx 3.3 = \text{p}K_a$; $K_a \approx 5 \times 10^{-4}$

(c) ≈ 8.5

65. (a) GT

(b) GT

(c) GT

(d) EQ

67. (a) False; $[\text{CHO}_2^-] = 0.1 \text{ M}$ only in 0.1 M NaCHO_2

(b) True

(c) False; combining a conjugate acid-base pair

(d) False; K_b for $\text{HCO}_3^- = 2.3 \times 10^{-8}$; K_b for $\text{CO}_3^{2-} = 2.1 \times 10^{-4}$

69. (a) acid (b) C (c) $\approx 10^{-8}$ (d) 0.1 (e) ≈ 5

70. at 1/3 neutralization, one mole of base is formed for every three moles of acid to be neutralized.

Thus two moles of acid are left.

$$[\text{H}^+] = 6.7 \times 10^{-4} \times \frac{2}{1} = 1.3 \times 10^{-3}; \quad \text{pH} = 2.9$$

$$71. 6.3 \times 10^{-5} = 1.8 \times 10^{-5} \times \frac{\text{mol HAc}}{\text{mol Ac}^-}; \quad \frac{\text{mol HAc}}{\text{mol Ac}^-} = 3.5$$

$$\text{mol OH}^- = (0.100 \text{ L})(1.25 \text{ mol/L}) = 0.125 = \text{mol Ac}^-; \quad \text{mol HAc for the buffer} = (3.5)(0.125) = 0.44$$

$$\text{mol HAc needed} = 0.125 \text{ (to form Ac}^-) + 0.44 \text{ (HAc needed in buffer)} = 0.56$$

$$V = [34 \text{ g HAc}(0.98)](1 \text{ mL}/1.0542 \text{ g}) = 33 \text{ mL}$$

72. pH of original solution = 2.56; $[\text{H}^+] = 2.8 \times 10^{-3}$;

$$K_a = 5.5 \times 10^{-5} \quad \text{At half-neutralization, pH} = 4.25$$

$$5.5 \times 10^{-5} = \frac{(2.8 \times 10^{-3})^2}{[\text{HA}]}; \quad [\text{HA}] = 0.14 \text{ M}$$

$$\text{mol HA} = (0.14 \text{ mol/L})(0.250 \text{ L}) = 0.034; \quad \text{MM HA} = (4.0 \text{ g})(0.034 \text{ mol}) = 1.2 \times 10^2 \text{ g/mol}$$

73. pH is 6.50; $[\text{H}^+] = 3.16 \times 10^{-7}$

$$[\text{H}^+] = K_a \times \frac{\text{mol NH}_4^+}{\text{mol NH}_3}; \quad 3.16 \times 10^{-7} = 5.6 \times 10^{-10} \times \frac{\text{mol NH}_4^+}{\text{mol NH}_3}; \quad \frac{\text{mol NH}_4^+}{\text{mol NH}_3} = 565$$

One would need 500 times as much NH_4^+ as NH_3 .

$$74. (a) \frac{[\text{H}^+]^2}{1.000} = 6.0 \times 10^{-4}; \quad [\text{H}^+] = 2.4 \times 10^{-2} \text{ M}; \quad \text{pH} = 1.61$$

$$(b) \text{pH} = \text{p}K_a = 3.22$$

$$(c) \text{mol NO}_2^- = (1.000 \text{ mol/L})(0.0500 \text{ L}) = 0.0500; \quad V_{\text{NaOH}} = \frac{0.0500 \text{ mol}}{0.850 \text{ mol/L}} = 0.0588 \text{ L}$$

$$V_{\text{tot}} = 0.0500 \text{ L} + 0.0588 \text{ L} = 0.109 \text{ L}; \quad [\text{NO}_2^-] = 0.0500 \text{ mol}/0.109 \text{ L} = 0.459 \text{ M}$$

$$\frac{[\text{OH}^-]^2}{0.459} = 1.7 \times 10^{-11}; \quad [\text{OH}^-] = 2.8 \times 10^{-6} \text{ M}; \quad \text{pOH} = 5.55; \text{pH} = 8.45$$

$$(d) \text{mol HNO}_2 \text{ left} = (1.0 \times 10^{-4} \text{ L})(0.850 \text{ mol/L}) = 8.50 \times 10^{-5}$$

$$[\text{H}^+] = 6.0 \times 10^{-4} \times \frac{8.50 \times 10^{-5}}{0.0500} = 1.0 \times 10^{-6} \text{ M}; \quad \text{pH} = 6.00$$

$$(e) \text{ mol OH}^- = (1.0 \times 10^{-4} \text{ L})(0.850 \text{ mol/L}) = 8.50 \times 10^{-5}$$

$$[\text{OH}^-] = \frac{8.50 \times 10^{-5} \text{ mol}}{0.109 \text{ L}} = 7.8 \times 10^{-4} \text{ M}; \quad \text{pOH} = 3.11; \text{ pH} = 10.89$$

(f) Similar to Figure 14.6 but pH is somewhat lower because HNO_2 is a stronger acid than $\text{HC}_2\text{H}_3\text{O}_2$.

$$75. 1.0 \times 10^{-5} = 1.8 \times 10^{-5} \times \frac{[\text{HC}_2\text{H}_3\text{O}_2]}{[\text{C}_2\text{H}_3\text{O}_2^-]}; \quad \frac{[\text{HC}_2\text{H}_3\text{O}_2]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = 0.56$$

$$\text{fraction neutralized} = \frac{1.00}{1.56} = 0.64; \quad 32 \text{ mL NaOH}$$

$$76. (a) [\text{H}^+] = 0.1500 \text{ M} \quad \text{pH} = 0.82$$

$$(b) 0.011 = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(0.1500 + x)(x)}{0.1500 - x}$$

Solving for x using the quadratic equation, $x \approx 0.01$; $[\text{H}^+] = 0.16 \text{ M}$; $\text{pH} = 0.80$

$$77. [\text{H}^+] = K_a \times \frac{[\text{HB}]}{[\text{B}^-]} = K_a \times \frac{7.00}{14.0}; \quad K_a = 2 [\text{H}^+] = 2(1.1 \times 10^{-9}); \quad K_b = \frac{1.0 \times 10^{-14}}{2.2 \times 10^{-9}} = 4.5 \times 10^{-6}$$

$$78. \text{ mol NH}_3 = (0.150 \text{ mol/L})(1.000 \text{ L}) = 0.150; \quad \text{mol NH}_4^+ = \text{mol NH}_4\text{Cl} = (10.0 \text{ g})(1 \text{ mol}/53.49 \text{ g}) = 0.187$$

$$[\text{H}^+] = 5.6 \times 10^{-10} \times \frac{0.187}{0.150} = 6.98 \times 10^{-10}; \quad \text{pH} = 9.16$$

$$\text{new pH} = 9.16 + 1.00 = 10.16; \quad [\text{H}^+] = 6.98 \times 10^{-11}$$

$$\text{Let } x = \text{mol OH}^- \text{ that react with NH}_3; \quad 6.98 \times 10^{-11} = 5.6 \times 10^{-10} \times \frac{0.187 - x}{0.150 + x}; \quad x = 0.15 \text{ mol OH}^-$$

$$\text{mass NaOH} = (0.15 \text{ mol})(40.0 \text{ g/mol}) = 6.0 \text{ g}$$

$$79. \log_{10} [\text{H}^+] = \log_{10} K_a + \log_{10} \frac{[\text{HB}]}{[\text{B}^-]}$$

$$\text{Multiply by } (-1): \text{ pH} = \text{p}K_a + \log_{10} \frac{[\text{B}^-]}{[\text{HB}]}$$